PATENT SPECIFICATION (11) 1247 189

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NO DRAWINGS

(21) Application No. 61003/68 (22) Filed 23 Dec. 1968

(31) Convention Application No. 55174 (32) Filed 28 Dec. 1967 in

(33) Luxembourg (LU)

(45) Complete Specification published 22 Sept. 1971

(51) International Classification C 11 d 1/02, 1/38, 1/66, 1/84, 3/04, 3/44

(52) Index at acceptance

C5D 6A5C 6A5D1 6B1 6B11A 6B11B 6B11C 6B11D 6B12A 6B12B1 6B12B2 6B12B3 6B12C 6B12E 6B12F1 6B12F2 6B12F4 6B12G2A 6B12G3 6B12G4 6B12G5 6B12G6 6B12K2 6B12L 6B12M 6B12N1 6B12N2 6B12P 6B15 6B2 6B3 6B4 6B5 6B6 6B8 6C8

D1P 1A3 1A4 1A5 1C3A 1C3B

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(54) LIQUID COMPOSITIONS FOR THE TREATMENT OF NATURAL OR SYNTHETIC FIBRES

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to liquid compositions for the treatment of natural fibres, and in particular for the cleansing or care thereof.

Liquid compositions for the treatment of hair in the form of one aqueous layer and one oily layer are known. It has also been proposed in British Patent Specification 1,133,870 to produce liquid detergent compositions comprising an aqueous detergent layer and an oily layer. Such compositions on shaking form a temporary oil-in-water emulsion and on standing separate again into two distinct layers. Colourants or dyes can be included in the separate layers to give products having an unusual and pleasing appearance.

However, such previously proposed products comprise an oily layer as an essential ingredient. We have now found that aqueous liquid compositions containing varying amounts of detergent and also existing in a plural-layer physical state but having two aqueous layers can be obtained by incorporating in a liquid composition containing 0.1 to 80% by weight of detergent an electrolyte and a water-miscible organic solvent in appropriate relative amounts.

Accordingly, therefore, the invention in its broadest aspect relates to a liquid detergent composition having a pH of from 4 to 7 suitable for the treatment of natural fibres containing from 0.1 to 80% by weight of a detergent, a water-miscible organic solvent, and an electrolyte, the relative proportions of the electrolyte and the organic solvent being such that the composition comprises two aqueous layers at 0°C.

The liquid composition of the invention may contain up to 90% by weight of the organic solvent but preferably contains an amount of the organic solvent of from 2 to 40% by weight of the composition. As the water-miscible organic solvent one may use, for example: a straight or branched chain monohydric aliphatic alcohol containing from 1 to 7 carbon atoms, such as ethyl alcohol or isopropyl alcohol; a dihydric aliphatic alcohol containing from 2 to 7 carbon atoms, such as hexylene glycol; a monoalkyl ether of an aliphatic dihydric alcohol containing a total of 3 to 6 carbon atoms, such as the monomethyl, -ethyl and -butyl ethers of ethylene glycol; or a dialkyl ketone containing a total of 3 to 5 carbon atoms, such as acetone. Other solvents that can be used are benzyl alcohol or phenyl ethyl alcohol. Preferred solvents are ethyl alcohol, hexylene glycol, the monomethyl ether of ethylene glycol, and acetone. Mixtures of solvents can also be used.

The amount of the solvent employed to some extent dictates the rate at which the layers in the products of the invention separate after shaking of the composition, which separation will usually occur between 5 minutes and 5 hours.

The relative proportions of the constituents of the liquid composition of the invention will usually be chosen in such a way that the weight of the lower aqueous layer is between 2% and 75% by weight of the composition.

In the liquid composition according to the

present invention, the amount of the electrolyte is preferably from 3 to 25% by weight of the composition.

The pH of the liquid composition may vary over a wide range between 4 and 7.

In a preferred form of the invention the electrolyte forms part of a buffering system.

Among the anionic constituents of the electrolytes may be cited: lactic acid, citric acid, tartaric acid, ascorbic acid, salicylic acid, phosphoric acid, ethylenediaminetetra-acetic acid, nitrilotriacetic acid, diethylene-triamine penta-acetic acid, 2 - hydroxyethyl-iminodiacetic acid, sorbic acid, glycollic acid, and mixtures of these acids. Among the cationic constituents may be cited sodium, potassium, lithium, ammonium, the alkanol-amines such as mono-, di-, and triethanol-amine and isopropylamine. Mixtures of different salts may of course be used. It is generally preferably to use electrolytes other than those with solely mineral cations, such as sodium or potassium citrate, or sodium or potassium phosphate, since the latter may provoke crystallisation leading to less attractive products.

The liquid compositions according to the present invention are very suitable for the cleansing or care of the hair.

It was found in washing tests on human hair that the application of a liquid composition of the invention in the form of a shampoo in which the electrolyte formed part of an acid buffering system, compared with that of the same shampoo without the electrolyte and organic solvent, produced certain beneficial effects, and in particular the gloss, softness and setting properties of the hair were improved and, in the case of greasy hair, a slowing down of the rate of becoming greasy again was obtained. These results were obtained in salon trials involving two groups of women totalling 50 in number, the majority of whom had greasy hair. The use of shampoos containing an acid buffering system has been found to be particularly advantageous when washing the hair with hard water, since the reserve of acidity prevents or reduces the deposition of calcium and magnesium soaps on the hair thereby improving the condition of the hair.

Moreover the action of certain bactericides is favourably influenced by an acid medium.

As already indicated, in the formation of a system of two aqueous layers, the amounts of the electrolyte and the organic solvent are inter-related. For a given detergent solution, the appropriate amounts of the electrolyte and the organic solvent can be determined by simple experiment. This relationship is illustrated below.

The influence of an increasing amount of electrolyte is demonstrated with the following system:

Ammonium lauryl sulphate	7.5% by weight
Hexylene glycol	25.0% by weight
Water	67.5% by weight

If one progressively replaces the water by an increasing amount of a solution of citric acid neutralized by monoethanolamine to pH 6.1, the system passes through three regions of different stabilities: —

a) With a concentration of the citric acid salt below about 9.5% by weight of the composition, the product is in the form of a homogeneous liquid.

b) On exceeding this concentration at room temperature (20°C), the product is in two layers. The upper layer contains the majority of the detergent, the lower layer contains the majority of the electrolyte. By shaking, one obtains a turbid product, which at room temperature in about half an hour again separates into two clear layers, one above the other. This system, however, is unstable since the volume of the layer containing the electrolyte is a function of the temperature and this layer disappears at relatively low temperatures (from 0°C to room temperature).

c) On further increasing the concentration of the citric acid salt to between 11 and 12% by weight, the two-layer system becomes stable, i.e., the two-layer physical state is obtained throughout the temperature range of the experiment.

The quantitative results are summarised in Table I below in which the weight percentage of the lower layer is indicated.

TABLE I

Percentage by weight of the composition of citric acid neutralized with monoethanolamine to pH 6.1	Weight percentages if lower layer at: 0°C	20°C	35°C	42°C
9	—	—	28%	38%
9.15	—	—	32%	39%
9.3	—	—	35%	40%
9.5	—	—	39%	42%
10	—	26%	42%	45%
11	—	45%	47%	48%
12	49%	49%	50%	50.5%
13	50%	51%	52%	52%

Similarly, the influence of an increasing amount of organic, water-miscible solvent is demonstrated with the following system:

Ammonium lauryl sulphate 7.5% by weight
Citric acid neutralized with monoethanolamine to pH 6.1 13.0% by weight
Water 79.5% by weight

If one progressively replaces the water in this system by hexylene glycol, one finds that:

a) with a concentration of hexylene glycol up to 13% by weight of the composition, the product is in the form of a clear and homogeneous liquid throughout the temperature range of 0 to 42°C;

b) with a concentration of 15% by weight of hexylene glycol the product is unstable, since at the higher temperatures of the temperature range it is in the form of two layers and at the lower temperatures it is homogeneous;

c) on increasing the concentration of hexylene glycol to 25% by weight of the composition, a stable two-layer system is produced. On exceeding 25% by weight of the hexylene glycol, the system remains stable and only the amount of the electrolyte layer is modified.

The quantitative results are summarised in Table II below, in which the weight percentage of the lower layer is again indicated.

TABLE II

Percentage by weight of the composition of hexylene glycol	Weight percentage of lower layer at: 0°C	20°C	35°C	42°C
13%	—	—	—	—
15%	—	—	50%	52%
25%	50%	51%	52%	52%
30%	48%	48%	48%	49%
35%	42%	43%	44%	44%

The detergent used in the liquid composition of the invention may be an anionic, cationic, non-ionic, or ampholytic detergent or a mixture thereof. The amount of the detergent in the composition is preferably between 5 and 30% by weight of the composition.

Examples of anionic detergents that may be used are: soaps of higher fatty acids containing from 8 to 26 carbon atoms; long-chain primary or secondary alkyl sulphates containing from 8 to 22 carbon atoms, such as lauryl sulphate; esters of sulphuric acid and polyols partially esterified with higher fatty acids, for example the monosulphate of tallow monoglyceride; sulphated alkanolamides of higher fatty acids; alkyl ether sulphates, for example lauryl ether sulphate; hydroxylsulphonated esters of higher fatty acids; esters of higher fatty acids and low-molecular-weight hydroxy alkanesulphonic acids, for example the oleic ester of isethionic acid; amides of higher fatty acids and aminoalkanesulphonic acids, for example the oleic amide of taurine; water-soluble alkyl phosphates; sulphated reaction products of alkylene oxides with hydrophobic materials as described below; sulphonated oils; sulphonated higher fatty acids; primary and secondary alkyl sulphates; olefin sulphonates; and sulphonates of alkylaromatic hydrocarbon compounds possessing an alkyl substituent containing from 8 to 26 carbon atoms (with a mono- or polynuclear structure).

Examples of cationic detergents are alkylamine salts; quaternary ammonium salts; and acylalkanolamine salts.

As non-ionic detergents that can be used in the compositions according to the present invention may be mentioned: condensation products of alkylene oxides with hydrophobic compounds such as higher fatty alcohols, polyols, alkylphenols, products of the reaction of propylene oxide with ethylenediamine, fatty acid amides, amides of alkanesulphonic acids, substituted polyamines, and polypropylene glycols. Other non-ionic products are the products of the condensation of fatty acid chlorides with hydrolysed natural proteins, esters of higher fatty acids and sugars.

The ampholytic detergents that can be used are, for example, salts of N-alkylated compounds of β-aminopropionic acid, imidazolines, betaines, and sultaines.

The detergents may be used in the form of their water-soluble salts such as the alkali metal, alkaline-earth metal, and ammonium salts, and also in the form of salts of nitrogen-containing bases such as the alkanolamines, for example mono-, di-, and triethanolamine. It is also possible to use mixtures of salts.

Also foam improvers and stabilisers may be included in the liquid composition of the invention. The foam improver and stabilizer, which will generally be a part of the detergent, may be used in a proportion of up to 50%, preferably between 2 and 25%, by weight of the composition. As foam improvers and stabilisers may be employed tertiary amine oxides, betaines, and higher fatty acid alkanolamides.

It is, of course, possible to include in the compositions of the present invention additives customarily used in the detergent and cosmetic industry, in particular perfumes (deterpenised or not), emollients, colouring agents, preservatives, protein hydrolysates, antioxidants, germicides, and pigments.

The liquid composition according to the invention may contain variable amounts of natural and synthetic liquid water-immiscible oily materials, for example, the weight percentage of the oily material may be up to 50% of the composition. Particularly suitable natural oily materials are light and heavy mineral or hydrocarbon oils, animal and vegetable oils, alkyl esters of fatty acids, and lanolin derivatives. It is also possible to use synthetic oily materials such as silicone oil of fairly high fluidity, particularly in the case where the composition is used for washing textiles, for which the silicone oil serves to provide a water-repellent finish. In the case where the composition contains a silicone oil and one or more vegetable, animal, or mineral oils, the composition at rest comprises, in addition to the two aqueous layers, two oily layers, since these two types of oil do not mix with one another.

The use of colouring agents ensures that the compositions according to the invention have a good appearance. In fact, colouring agents soluble in aqueous media are preferentially distributed between the two aqueous phases and, when oily phases are present, oli-soluble colouring agents are likewise distributed preferentially in the various oily phases. This leads to the situation that the composition according to the invention when at rest has the form of a superposition of two or more layers of different colours.

To obtain the coloration of the different layers, it is preferable to dissolve colouring agents soluble in the aqueous media in the aqueous phases alone and then to dissolve the lip soluble colouring agent or agents separately in the oily phase or phases alone, and subsequently to mix the aqueous and the oily phases together.

The liquid products according to the present invention may be in the form of, for example, shampoos, and foam baths.

As mentioned above, the liquid compositions according to the present invention are shaken before use to form an intimate mixture. An acceptable dose for use as a shampoo, for instance, is about 7 to 30 g. per shampooing.

The invention will now be illustrated by the following Examples of liquid detergent composition comprising two layers of 0°C in accordance with the invention in which the percentages given are percentages by weight.

EXAMPLE 1

The following mixture is made:

	%
Ammonium lauryl sulphate	14.0
Coconut diethanolamide	6.0
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	4.0
Hexachlorophene	0.5
Hexylene glycol	10.0
Perfume	0.5
Neutral monoethanolamine citrate	16.5
Citric acid	3.0
Sorbic acid	0.2
Water, colouring agents, etc.	45.3

This composition has a pH between 5 and 6. After being shaken and left for some hours, the composition separates into two distinct layers: 42% by weight of lower layer and 58% by weight of upper layer. This composition is particularly useful for the care of the hair.

EXAMPLE 2

The following mixture is made:

	%
Ammonium lauryl sulphate	12.3
Coconut diethanolamide	5.3
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	3.5
Hexylene glycol	13.0
Perfume	2.0
Neutral monoethanolamine citrate	14.5
Citric acid	2.7
Water, colouring agents, etc.	46.7

This composition has a pH between 5 and 6. After being shaken and left for some hours, the composition separates into two distinct layers: 37% by weight of lower layer and 63% by weight of upper layer. This composition is particularly useful as a perfumed foam bath.

EXAMPLE 3

The following mixture is made:

	%
Sodium lauryl ether sulphate with 2 molecules of ethylene oxide	12.5
Coconut diethanolamide	9.0
Hexylene gycol	14.0
Perfume	0.5
Neutral monoethanolamine citrate	13.0
Citric acid	3.0
Water, colouring agents, etc.	48.0

This composition has a pH between 5 and 6. After being shaken and left for some hours, the composition separates into two distinct layers: 22% by weight of lower layer and 78% by weight of upper layer. This composition is particularly useful for washing woollen goods.

EXAMPLE 4

The following mixture is made:

	%
Ammonium lauryl sulphate	13.5
Coconut diethanolamide	6.0
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	4.0
Hexachlorophene	0.5
Alkyldimethylbenzylammonium saccharinate	0.5
Hexylene glycol	15.0
Perfume	0.5
Neutral monoethanolamine citrate	12.0
Citric acid	2.0
Water, colouring agents, etc.	46.0

This composition has a pH between 5 and 6. After being shaken and left for some hours, the composition separates into two distinct layers: 44% by weight of lower layer and 56% by weight of upper layer. This composition is particularly useful as an anti-dandruff shampoo.

EXAMPLE 5

The following mixture is made:

	%
Ammonium lauryl sulphate	12.0
Coconut diethanolamide	6.0
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	4.0
Sodium salt of monoethanolamine undecylenic sulphosuccinate	2.0
Hexachlorophene	0.5
Hexylene glycol	15.0
Perfume	0.5
Neutral monoethanolamine citrate	14.0
Citric acid	2.0
Water, colouring agents, etc.	44.0

This composition has a pH between 5 and 6. After being shaken and left for several hours, the composition separates into two distinct layers: 35% by weight of lower layer and 65% by weight of upper layer. This composition is particularly useful as an anti-dandruff shampoo.

Below, three possibilities for colouring the detergent composition described in this example are given:

1) For each 100 g of composition, 0.0015 g of blue dye (Colour Index No. 42051) and 0.0025 g of yellow dye (Colour Index No. 19140) are added to the two aqueous phases. The emulsified product has a pale green opalescent colour. On standing, it separates into two layers; the upper layer is green and the lower layer is lemon-yellow.

2) For each 100 g of composition, 0.0025 g of orange dye (Colour Index No. 15510) and 0.0050 g of yellow dye (Colour Index No. 19140) are added to the two aqueous phases. The emulsified product has an orange opales-

cent colour. On standing, it separates into two layers; the upper layer is orange and the lower layer is golden yellow.

3) For each 100 g of composition, 0.0040 g of red dye (Colour Index No. 16255), 0.0030 g f red dye (Colour Index No. 16185), and 0.0025 g of yellow dye (Colour Index No. 19140) are added to the two aqueous phases. The emulsified product has a red opalescent colour. On standing, it separates into two layers: the upper layer is red and the lower layer is golden yellow.

EXAMPLE 6

The following mixture is made:

	%
Miranol HSC (Trademark: an amphopolytic detergent)	10.00
Alkyldimethylbenzylammonium chloride	0.10
Isoquinoline alkyl bromide	0.45
Coconut diethanolamide	7.50
Hexylene glycol	2.00
Neutral monoethanolamine citrate	15.00
Citric acid	3.00
Perfume	0.50
Water, colouring agents, etc.	61.45

This composition has a pH of 5. After being shaken and left for some hours, the composition separates into two distinct layers: 29% by weight of lower layer and 71% by weight of upper layer. This composition is particularly useful as a shampoo.

EXAMPLE 7

The following mixture is made:

	%
Ammonium lauryl sulphate	14.0
Coconut diethanolamide	5.0
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	5.0
Acetone	12.0
Hexachlorophene	0.5
Neutral monoethanolamine citrate	15.0
Citric acid	2.0
Perfume	0.5
Water, colouring agents, etc.	46.0

This composition has a pH between 5 and 6. After being shaken and left for 2 hours, the composition separates into two distinct layers: 25% by weight of lower layer and 75% by weight of upper layer. This composition is particularly useful as a shampoo for dry hair.

EXAMPLE 8

The following mixture is made:

	%
Ammonium lauryl sulphate	5.0
Coconut diethanolamide	5.0
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	5.0
Methylcellosolve (Trademark: monomethyl ether of ethylene glycol)	10.0
Neutral monoethanolamine citrate	15.0
Citric acid	2.0
Perfume	0.5
Water, colouring agents, etc.	57.5

This composition has a pH between 5 and 6. After being shaken and left for 6 hours, the composition separates into two distinct layers: 10% by weight of lower layer and 90% by weight of upper layer. This composition is particularly useful as a shampoo.

EXAMPLE 9

The following mixture is made:

	%
Ammonium lauryl sulphate	5.35
Hexylene glycol	39.50
Sodium chloride	7.15
Perfume	0.50
Water, colouring agents, etc.	47.5%

This composition has a pH of 7. After being shaken and left for half an hour, the composition separates into two distinct layers: 22% by weight of lower layer and 78% by weight of upper layer.

EXAMPLE 10

The following mixture is made:

	%
Sodium lauryl ether sulphate with 2 molecules of ethylene oxide	16.0
Lauryldimethyl amine oxide	3.5
Ethyl alcohol	10.0
Citric acid	3.0
Potassium citrate	15.0
Perfume	0.5
Water, colouring agents, etc.	52.0

This composition has a pH of 5.3. After being shaken and left for some hours, the composition separates into two distinct layers: 34% by weight of lower layer and 66% by weight of upper layer. This composition is particularly useful as a shampoo.

EXAMPLE 11

The following mixture is made

	%
Ammonium lauryl sulphate	10.5
Coconut diethanolamide	5.0
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	3.0
Sodium salt of a dicarboxylic lauryl derivative.	4.0
Sodium salt of monoethanolamine undecylenic sulphosuccinate	2.0
Alkyldimethylbenzylammonium saccharinate	0.5
Neutral monoethanolamine tartrate	10.0
Lactic acid	1.0
Fluid paraffin oil	10.0
Perfume	0.5
Hexylene glycol	15.0
Water, colouring agents, etc.	38.5

As the fluid paraffin oil, an oil having a density at 20°C between 0.835 and 0.855 is used.

A composition is obtained with a pH

between 5 and 6 when it is emulsified. After being emulsified and left for some hours, the composition has the form of three separate layers: 22% by weight of lower layer, 70.5% by weight of intermediate layer, and 7.5% by weight of oily upper layer. This composition is particularly useful as an antidandruff shampoo treatment for normal hair.

EXAMPLE 12

The following mixture is made:

	%
Ammonium lauryl sulphate	12.0
Coconut diethanolamide	6.0
Ethoxylated lauryl alcohol with 7 molecules of ethylene oxide	4.0
Monoethanolamine citrate	10.0
Citric acid	2.0
Fluid paraffin oil	10.0
Silicone oil (viscosity 100—200 centistokes)	5.0
Perfume	0.5
Hexylene glycol	15.0
Water, colouring agents, etc.	35.5

The fluid paraffin oil is the same as used in Example 15.

A composition is obtained with a pH between 5 and 6 when it is emulsified. After being emulsified and left for some hours, the composition has the form of four distinct layers: 26% by weight of lower layer, 63% by weight of second aqueous layer, 4% by weight of first oily layer and 7% by weight of oily upper layer. This composition is particularly useful for the washing of fabric whereby hydrophobic properties are imparted to the fabric.

WHAT WE CLAIM IS:—

1. A liquid detergent composition having a pH of from 4 to 7 suitable for the treatment of natural fibres containing from 0.1 to 80% by weight of a detergent, a water-miscible organic solvent, and an electrolyte, the relative proportions of the electroyte and the organic solvent being such that the composition comprises two aqueous layers at 0°C.

2. A liquid composition as claimed in Claim 1, wherein the amount of the water-miscible organic solvent is from 2 to 40% by weight of the composition.

3. A liquid composition as claimed in Claim 1 or Claim 2, wherein the water-miscible organic solvent is a straight or branched chain monohydric aliphatic alcohol containing from 1 to 7 carbon atoms; a dihydric aliphatic alcohol containing from 2 to 7 carbon atoms; a monoalkyl ether of an aliphatic dihydric alcohol containing a total of 3 to 6 carbon atoms or a dialkyl ketone containing a total of 3 to 5 carbon atoms.

4. A liquid composition as claimed in Claim 3, wherein the solvent is ethyl alcohol; hexylene glycol; the monomethyl ether of ethylene glycol or acetone.

5. A liquid composition as claimed in any one of the preceding claims, wherein the amount of the electrolyte is from 3 to 25% by weight of the composition.

6. A liquid composition as claimed in any one of the preceding Claims, wherein the electrolyte forms part of a buffering system.

7. A liquid composition as claimed in Claim 6, wherein the buffering system is a mixture of citric acid and an alkanolamine salt of citric acid.

8. A liquid composition as claimed in any one of the preceding Claims, wherein the amount of the detergent is from 5 to 30% by weight of the composition.

9. A liquid composition as claimed in any one of the preceding Claims, wherein the detergent comprises an anionic detergent.

10. A liquid composition as claimed in any one of the preceding Claims, wherein the detergent is an akyl sulphate or an alkyl ether sulphate.

11. A liquid composition as claimed in any one of the preceding Claims, wherein the composition also comprises a layer of a liquid, water-immiscible, oily material.

12. A liquid composition as claimed in Claim 11, wherein the oily material is a mineral oil.

13. A liquid composition substantially as herein described with reference to any one of Examples 1 to 12.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.